

heated in a mixed solvent of propionic acid (98.4 g) and propionic anhydride (91.0 g) at 103 °C for 7.5 h under nitrogen. After the treatment described above, cinnamic acid (324 mg, 5.0%), 1,4-diphenylbutadiene (380 mg, 9.0%), and β -propioxy styrene (1.5 g, 44%) were isolated.

Acknowledgment. The authors are indebted to Mr. H. Miyamoto and Miss Y. Sato for the NMR measurements, to Miss J. Maenaka and Mr. and Mrs. K. Muneishi for the elemental analyses, and also to Mr. H. Moriguchi for the mass analyses.

Registry No.—A, 31168-61-3; palladium(II) chloride, 7647-10-1; sodium malonate, 23549-97-5; palladium(II) acetate, 3375-31-3; styrene, 100-42-5; sodium acetate, 127-09-3; phenylallylic acid, 2243-53-0; 1,4-diphenylbutadiene, 886-65-7; β -acetoxystyrene, 10521-96-7; PhHgCl, 100-56-1; PhHgOAc, 62-38-4.

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 - (7) The formation of this compound has been previously communicated: T. Sakakibara, T. Teramoto, and Y. Odaira, *Chem. Commun.*, 1563 (1970).
 - (8) In the competitive reaction of benzene and benzene- d_6 , some different isotope effect was observed between palladium(II) malonate salt (A) and palladium(II) acetate. Namely, the formation ratio of benzoic acid and benzoic acid- d_6 was 3.9 with A, 4.4 with the latter.
- A: $\frac{\text{benzene-COOH}}{\text{benzene-}d_6\text{-COOH}} = 3.9$

Pd(OAc)₂: $\frac{\text{benzene-COOH}}{\text{benzene-}d_6\text{-COOH}} = 4.4$
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Synthesis of 4-Lithio-2-methyl-2-pentene. A New Type of Allylic Organometallic Compound¹

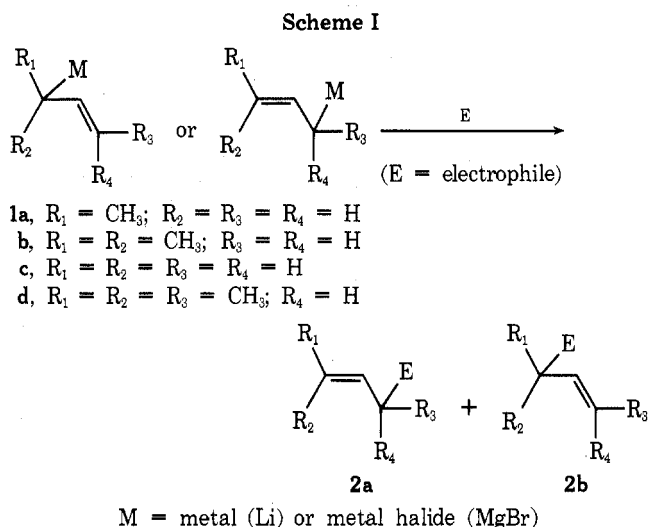
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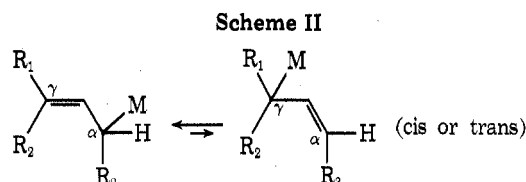
Received August 5, 1975

Allylic organometallics have long been the subject of intensive investigation.² In particular, the ability of unsymmetrical allylic organometallics (1) to attach themselves to electrophiles by either end of the allylic system (2a and 2b) (Scheme I) has interested many workers. The nature of some electrophiles (alkyl halide, mineral acid, carbon dioxide) can greatly affect the ratio of these two possible product types.³ It is, therefore, difficult to say anything about the point of attachment of the metal in the organometallic species unless some physical method such as NMR is used as a probe.

Fortunately, much NMR work has been done and compounds such as 2-butenyl (crotyl)⁴ (1a), 2-methyl-2-butenyl⁵ (1b), and propenyl (allyl)⁶ (1c) Grignard reagents have been investigated. In each of the above cases where the allylic sys-



tem is unsymmetrical (1a and 1b), the organometallic compound has been shown to be a rapidly interconverting mixture of isomeric compounds (Scheme II). The predominant isomer



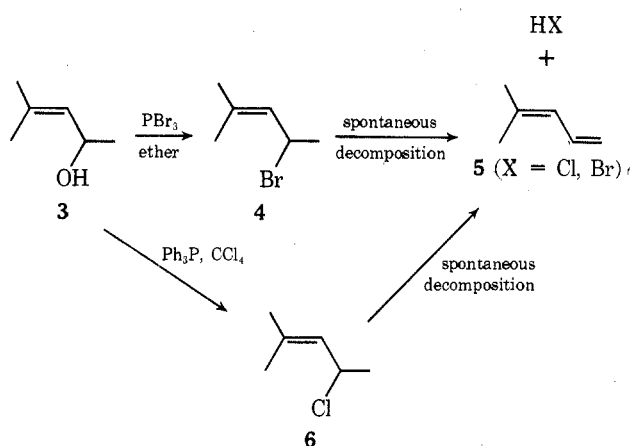
is always the isomer in which the metal is attached to the *least* substituted end of the allylic system (herein termed the α carbon).^{4,5} The isomer with metal attached to the most substituted carbon (herein termed the γ carbon) is presumably present in only small quantities at room temperature.⁵

To date, all investigation concerning unsymmetrical allylic organometallics where all the nonhydrogen substituents on the α and γ carbons are alkyl has been with systems where the point of metal attachment may be either on a primary or secondary allylic carbon (crotyl and related systems) or a primary or tertiary allylic carbon (2-methyl-2-butenyl and related systems). No simple allylic organometallic in which the position of attachment of the metal atom may be on either a secondary and tertiary allylic carbon has been synthesized and studied. We now wish to report the synthesis of such a system, namely 4-lithio-2-methyl-2-pentene (1d), and the results of several reactions of this new organometallic with several carbonyl compounds.

Generally, the synthesis of allylic organometallics can easily be effected from the corresponding bromide or chloride. With this in mind, we attempted to synthesize 4-bromo-2-methyl-2-pentene (4) from 2-methyl-2-penten-4-ol (3) using phosphorus tribromide in ether (Scheme III), a method reported by Roberts and co-workers for the synthesis of 4.^{7a} The results of this attempt were disappointing as the bromide spontaneously decomposed to give HBr and what NMR studies indicated to be 4,4-dimethyl-1,3-butadiene (5). The report by Roberts is, it should be noted, the only reference in the chemical literature to the synthesis of 4.^{7b} Similar results were obtained when the synthesis of 4-chloro-2-methyl-2-pentene (6) was attempted using 3 and a mixture of triphenylphosphine and carbon tetrachloride, a method reported to be suitable for the synthesis of allylic chlorides which are prone to rearrangement.⁸ Presumably, the extreme difficulty of obtaining these halides in pure form under normal conditions accounts for the fact that the corresponding allylic anion (1d) and related systems have not been prepared.

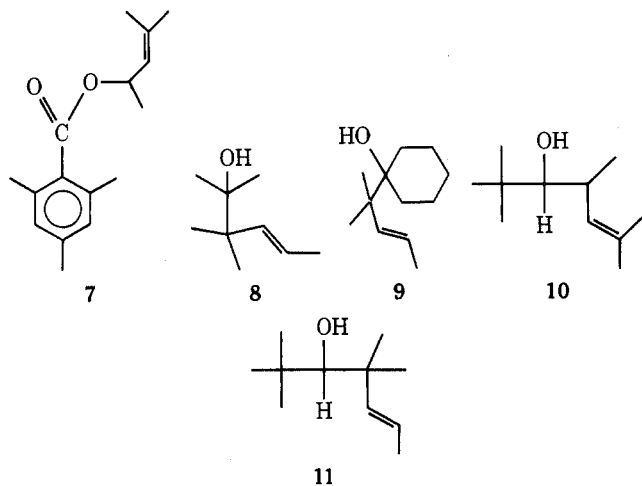
Mesitoate esters of allylic alcohols, however, have been

Scheme III



shown to be good in situ sources of allylic anions when treated with lithium metal in tetrahydrofuran in the presence of allylic halides, aldehydes, or ketones.⁹ The mesitoate ester of 3, 4-(2-methyl-2-pentenyl) mesitoate (7), was therefore prepared by treating that alcohol with mesityl chloride in chloroform.⁹ Since reaction of the resulting in situ generated allyllithium with electrophile is extremely rapid, this method of synthesis precluded NMR study of organolithium 1d, which originally had been one of our goals.

Anion 1d was accordingly generated from the mesitoate ester 7 in the presence of three carbonyl compounds: the unhindered ketones acetone and cyclohexanone and the hin-



dered aldehyde 2,2-dimethylpropanal. The results of these reactions are summarized in Table I.

Table I. Reaction of 4-Lithio-2-methyl-2-pentene with Carbonyl Compounds

Registry no.	Carbonyl compd	Products (ratio)	% yield of carbinol(s)
67-64-1	Acetone	8	49
108-94-1	Cyclohexanone	9	35
630-19-3	2,2-Dimethylpropanal	10, 11(1:2)	83

It is interesting to note that reaction of anion 1d with the unhindered ketones acetone and cyclohexanone gave carbinol products 8 and 9, respectively, in which the allylic system is attached by the *most* substituted end of the system (γ carbon). This similarity of behavior with the 1-butenyl and 2-methyl-2-butenyl systems which also react with unhindered ketones to produce carbinols in which the allylic system is

attached by the γ carbon may indicate that the organometallic reagent 1d has the lithium atom attached to the *least* substituted end of the allylic system (α carbon).

Reaction of 1d with the more hindered substrate 2,2-dimethylpropanal gave slightly different results. It can be seen in Table I that one of the reaction products, compound 10, has the allylic unit attached by the *least* substituted end (α carbon) of the allylic system. This type of behavior is similar to that reported by Benkeser and co-workers for the reaction of crotyl Grignard (1a) with the very hindered carbonyl electrophile di-*tert*-butyl ketone.¹⁰ These workers reported that although the most rapidly formed (least stable) product had the butenyl (crotyl) system attached by the most substituted end of the allylic system (δ carbon), the more stable product had the allylic unit attached by the least substituted end of the system (α carbon).¹¹ The product ratio was found to change with time, with the least stable product disappearing almost entirely after 192 h. In the reaction of 1d with 2,2-dimethylpropanal, the ratio of products 10 and 11 always was 1:2, respectively, regardless of when the reaction mixture was examined. Isolation of pure 10 followed by treatment with lithium metal in tetrahydrofuran led in a very short period of time to a 1:2 mixture of 10 and 11. This indicates that the product ratio observed is a result of thermodynamic as opposed to kinetic control; the establishment of equilibrium must be extremely rapid.

In contrast to anion 1d, the 2-methyl-2-butenyl anion (1b) can be generated in the presence of 2,2-dimethylpropanal from the corresponding bromide (12) using either magnesium¹¹ or lithium¹² metal. When this was done, the only product found was 3,3,5,5-tetramethyl-1-hexen-4-ol (13) in which the allylic

unit is attached by the *most* substituted end (γ carbon) of the allylic system. This would indicate that the behavior observed for anion 1d and 2,2-dimethylpropanal is due to increased steric hindrance in the more highly substituted allylic anion 1d.

We have assigned *E* (trans) geometry to the double bond in carbinols 8 and 9 as well as compound 11. Examination of the vinyl region of the NMR spectrum of these compounds showed a coupling constant for the vinyl protons of 12.5 Hz, a value which makes it difficult to assign geometry. However, strong infrared absorption in the 960–985- cm^{-1} region indicated that the samples were *E* isomers. If the transition state leading to the carbinol product resembles the product itself, then the preference for trans geometry is clear as that geometry in products 8, 9, and 11 should result in a more thermodynamically stable product than would cis geometry.

Experimental Section

General. 2-Methyl-2-penten-4-ol (3) was prepared by lithium aluminum hydride reduction of mesityl oxide in dry tetrahydrofuran. The alcohol was purified by distillation (137–139 °C, 747 Torr). Mesityl chloride was prepared by treating mesitoic acid with thionyl chloride.¹³ 2,2-Dimethylpropanal and 2-methyl-4-bromo-2-butene (12) were purchased from Chemical Samples Co. Lithium wire (0.1% Na) was obtained from Ventron and was washed in hexane prior to use.

All NMR spectra were recorded on a Varian T-60 instrument with Me_4Si as an internal standard. IR spectra were recorded on a Beckman IR-8. Microanalyses were performed by the University of Illinois. All preparative gas chromatography was done on a column of 15% Carbowax 20M on 60–80 mesh Chromosorb W.

4-(2-Methyl-2-pentenyl) Mesitoate (7). The ester was prepared in 79% yield from alcohol 3 and mesityl chloride:⁹ bp 124–126 °C (0.13 Torr); ir (neat) 2980 (m), 2940 (m), 1755 (s), 1630 (m), 1450 (m),

1380 (m), 1272 (s), 1175 (s), 1088 (s), 855 cm^{-1} (m); NMR (CCl_4) δ 1.30 (d, $J = 6$ Hz, 3 H), 1.78 (m, 6 H), 2.22 (s, 9 H), 5.20 (d, $J = 10$ Hz, 1 H, vinyl), 5.50–6.05 (m, 1 H), 6.70 (s, 2 H, aromatic).

Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{O}_2$: C, 77.99; H, 9.00. Found: C, 77.86; H, 8.93.

Reaction of Mesitoate Ester 7 with Carbonyl Compounds. The ester (0.05 mol) and the carbonyl compound (0.05 mol) were allowed to stir in 50 ml of dry THF with an excess (0.5 mol) of lithium metal. When all of the ester was consumed (TLC), the reaction was quenched and a standard aqueous workup employed to isolate the carbinol product(s). Pure samples were prepared by preparative GLC.

Reaction with Acetone. Compound 8: 49% yield; ir (neat) 3520 (s), 3020 (w), 2960 (s), 1610 (w), 980 cm^{-1} (s); NMR (CCl_4) δ 1.00 (s, 6 H), 1.07 (s, 6 H), 1.75 (d, $J = 5$ Hz, 3 H), 4.60 (s, 1 H, -OH), 5.58 (m, 2 H, vinyl).

Anal. Calcd for $\text{C}_9\text{H}_{18}\text{O}$: C, 75.98; H, 12.76. Found: C, 75.83; H, 12.82.

Reaction with Cyclohexanone. Compound 9: 35% yield; ir (neat) 3500 (s), 3040 (s), 2900 (s), 1630 (m), 1450 (s), 1380 (s), 1320 (m), 1270 (s), 1138 (s), 982 (s), 852 cm^{-1} (m); NMR (CCl_4) δ 1.00 (s, 6 H), 1.47 (s, 10 H), 1.76 (d, $J = 5$ Hz, 3 H), 2.33 (s, 1 H, -OH), 5.58 (m, 2 H, vinyl).

Anal. Calcd for $\text{C}_{12}\text{H}_{22}\text{O}$: C, 79.04; H, 12.17. Found: C, 78.97; H, 12.08.

Reaction with 2,2-Dimethylpropanal. Compounds 10 and 11, 83% yield overall, 1:2 ratio, respectively.

Compound 10: ir (neat) 3500 (s), 2900 (s), 2870 (s), 1670 (s), 1480 (s), 1445 (s), 1360 (s), 1080 (s), 980 (s), 840 cm^{-1} (s); NMR (CCl_4) δ 0.90 (s, 9 H), 1.00 (d, $J = 6$ Hz, 3 H), 1.40 (s, 1 H, -OH), 1.67 (m, 6 H), 2.20 (m, 1 H), 3.10 (d, $J = 3$ Hz, 1 H), 5.20 (d, $J = 9$ Hz, 1 H).

Anal. Calcd for $\text{C}_{11}\text{H}_{22}\text{O}$: C, 77.56; H, 13.03. Found: C, 77.42; H, 12.71.

Compound 11: ir (neat) 3510 (s), 3045 (m), 2900 (s), 1665 (w), 1460 (s), 1265 (m), 1140 (s), 980 cm^{-1} (s); NMR (CCl_4) δ 0.95 (s, 9 H), 1.10 (s, 6 H), 1.68 (d, $J = 4.5$ Hz, 3 H), 2.30 (s, 1 H), 3.00 (s, 1 H, -OH), 5.42 (m, 2 H, vinyl).

Anal. Calcd for $\text{C}_{11}\text{H}_{22}\text{O}$: C, 77.56; H, 13.03. Found: C, 77.76; H, 12.82.

3,3,5,5-Tetramethylhexen-4-ol (13). 2,2-Dimethylpropanal (0.05 mol) and 2-methyl-4-bromo-2-butene (12, 0.05 mol) were treated in dry THF with an excess of magnesium¹¹ or lithium.¹² Following a standard aqueous workup, the carbinol product 13 was distilled (109–110 °C, 30 Torr). Yield in both cases was approximately 82%; ir (neat) 3500 (s), 3090 (w), 2970 (s), 2880 (s), 1632 (w), 1480 (m), 1365 (m), 1050 (s), 1005 (s), 987 (s), 905 cm^{-1} (s); NMR (CCl_4) δ 1.00 (s, 9 H), 1.18 (s, 6 H), 2.00 (s, 1 H), 3.08 (s, 1 H, -OH), 4.78–5.10 (m 2 H) 6.02 (d of d, $J_a = 19$, $J_b = 10$ Hz, 1 H).

Anal. Calcd for $\text{C}_{10}\text{H}_{20}\text{O}$: C, 76.84; H, 12.91. Found: C, 76.57; H, 12.83.

Acknowledgment. The authors thank Research Corporation for their assistance in the form of a Cottrell College Science Grant.

Registry No.—1d, 58602-59-8; 3, 4325-82-0; 7, 58602-60-1; 8, 58602-61-2; 9, 58602-62-3; 10, 58602-63-4; 11, 58602-64-5; 12, 870-63-3; 13, 58602-65-6; mesityl oxide, 141-79-7; mesityl chloride, 938-18-1.

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Tetrabenzylethylene. An Unusually Sterically Hindered Olefin

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Received December 16, 1975

Current interest in the properties of sterically hindered olefins¹ prompts us to report our results with tetrabenzylethylene (1). In the course of an attempt to prepare a bromohydroperoxide from 1, we found that 1 was rather inert to the addition of bromine in carbon tetrachloride.² Similarly, 1 was inert to potassium permanganate solution² over a 25-min period as well as being inert to 2,4-dinitrobenzenesulfonyl chloride² and mercuric acetate.³ The well-known inertness of tetraphenylethylene⁴ is usually attributed solely to resonance stabilization of the olefinic bond. However, in view of the inert behavior of 1, the steric effect of four phenyl groups in close proximity to the olefinic bond may be sufficient for inert behavior.

In order to assess the steric effects in 1, the rate of bromination in acetic acid at 24.0 °C was measured by an iodometric method.⁵ A second-order rate coefficient of $8.68 \pm 0.29 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ was obtained with the reaction mixture under a nitrogen blanket and protected from light. A considerable amount of rate data obtained by Robertson and co-workers for bromination of olefins under these conditions has been compiled.⁶ Most of these rates can be correlated with the Taft polar effect equation (eq 1)

$$\log k = \rho^* \Sigma \sigma^* + a_0 \quad (1)$$

where $\rho^* = -2.58 \pm 0.099$, and $a_0 = 4.85 \pm 0.25$ with r (correlation coefficient) = 0.992. With these values for eq 1, the calculated bromination rate of 1 is $4.28 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ at 24 °C. Thus, steric effects in 1 causes a reduction in rate of about 5×10^5 -fold ($= 4.28 \times 10^2 / 8.68 \times 10^{-4}$).

Dubois and Mouvier⁷ reported the rates of bromination of olefins in methanol at 25 °C with 0.2 M sodium bromide, where steric effects in a few olefins were significant. These data are best correlated with the Taft polar-steric effect equation (eq 2)

$$\log k = \rho^* \Sigma \sigma^* + \delta \Sigma E_s + a_0 \quad (2)$$

where $\rho^* = -5.30$, $\delta = 0.913$, and $a_0 = 5.64$ with $r = 0.999$.⁸ To compare our data in acetic acid at 24 °C to the data of Dubois and co-workers in methanol at 25 °C, we have calculated the relative rate of bromination of 1 in methanol ($1.52 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$) to acetic acid ($4.28 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$) where polar effects alone correlate the data.⁸ With this factor ($1.52 \times 10^3 / 4.28 \times 10^2 = 3.55$), our experimental rate coefficient in acetic acid becomes $3.08 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ($= 3.55 \times 8.68 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$) in methanol. Now a calculated value of the rate of bromination of 1, with eq 2 and the parameters from the data of Dubois and Mouvier,⁷ is $4.91 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$. The experimental rate for 1 is then about 160-fold slower than predicted ($4.91 \times 10^{-1} / 3.08 \times 10^{-3} = 160$). Inclusion of 1 into a correlation of the data of Dubois and Mouvier⁷ by eq 2 gives a larger δ value; $\rho^* = -6.55$, $\delta = 1.41$, and $a_0 = 5.70$ with $r = 0.990$. This may be a more reliable correlation, since it extends the range of E_s values of the olefins by including 1.⁹

An examination of space-filling molecular models suggests that 1a is a low-energy conformation of tetrabenzylethylene. Previously, ¹H NMR studies of tetraisopropylethylene indicated a "cogwheel" effect with a high barrier to rotation, which involved conformation 2.¹ Two distinct tertiary protons were observed due to their disposition about the olefinic bond. Since conformation 1a suggests unique protons, the ¹H NMR